Adapting SAPRC Model Chemistry Mechanism to Low Temperature Conditions for Simulating Winter Ozone in Uintah Basin

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ACKNOWLEDGMENTS

Utah Department of Environmental Quality
Utah Energy Research Triangle
Bureau of Land Management – Utah Office

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July 28, 2015

Introduction -- Why Models Are Important

- Measurements are expensive (labor + equipment). We can use models to fill in the gaps.

- Models are used to inform regulatory decisions.

Introduction -- Models have three important components.

- Meteorology (wind patterns, temperature, humidity, …)
- Emissions Inventory (when, where, and how much of each pollutant entering the atmosphere)
- Chemistry (the "chemistry mechanism" = a mathematical modeling package of all possible reactions between all trace gases, as powered by ultraviolet radiation)

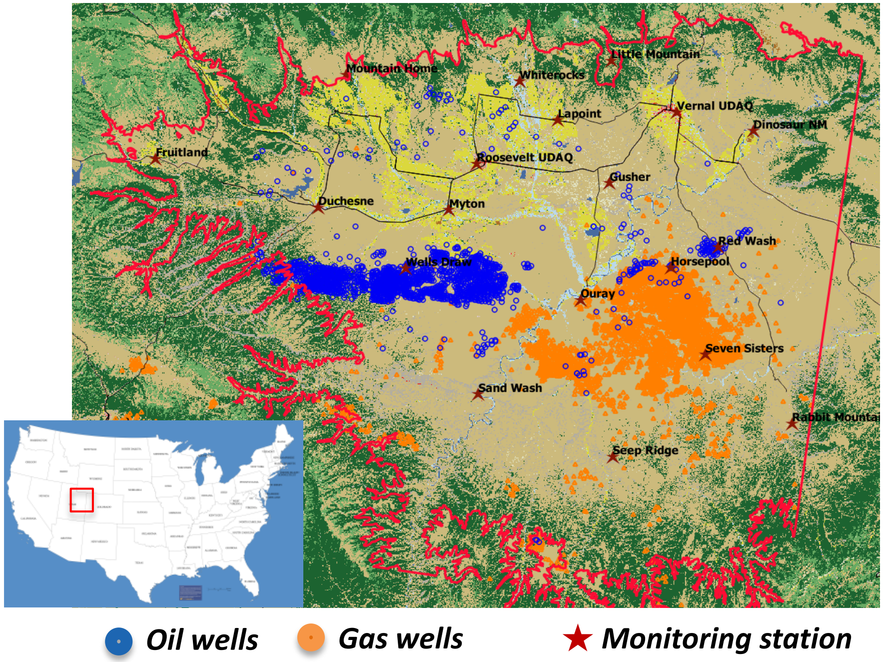
Introduction

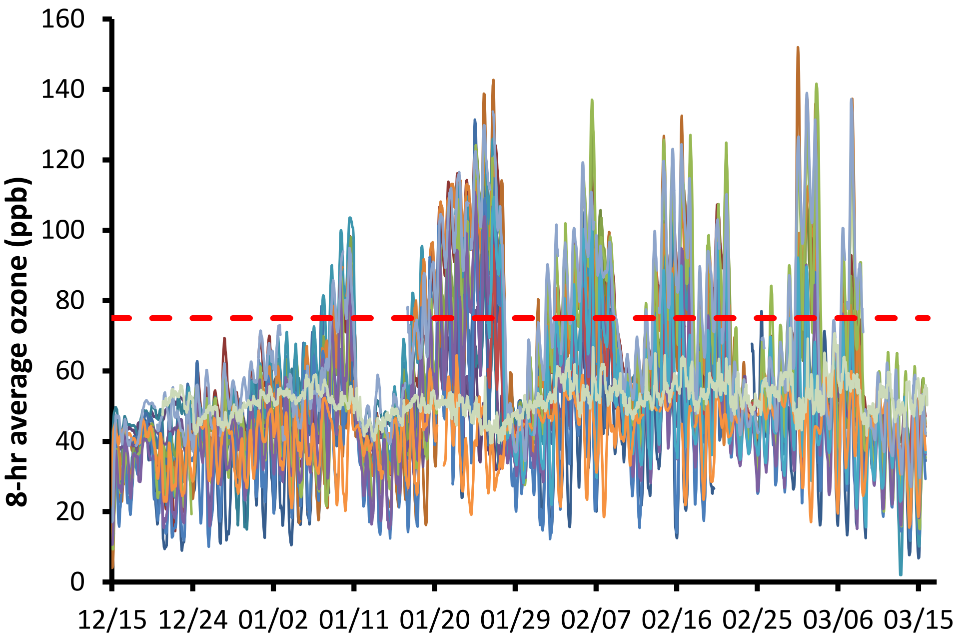
- Statement of Problem: Is the SAPRC07 Chemical Mechanism adequate for low- temperature, low-humidity work?
- Methodology: Identify missing or poorly represented reactions, then up-date the codes.
- Result: The updated models produce a net decrease in predicted ozone concentration.

Introduction

- Ozone pollution in the Uintah Basin, UT commonly occurs in wintertime when temperatures range between 260-270 K. Model chemical mechanisms were typically developed for studying ozone pollution in urban areas during summertime at a reference temperature of 300 K.
- Many chemical reactions that are negligible under summertime conditions become important for ozone formation under wintertime conditions.
- New measurements on chemical reactions became available but not all of them had been updated into the chemical mechanisms for photochemical models.

The chemical mechanisms need to be updated and adapted to low temperature conditions for better winter ozone photochemical model performance.





Methodologies

- Most intuitive way: smog chamber experiments under Uintah basin winter conditions. (Beyond the scope of this study)
- Literature review to capture most up-to-date results
  - NASA Jet Propulsion Laboratory: *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*. Latest update: Evaluation 17 (2011)
  - IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation. Latest date July 2014.
  - Other published peer-reviewed journal articles

<u>Mechanism of interest:</u>

Statewide Air Pollution Research Center 2007 (**SAPRC07**)

Improvements made to SAPRC07 mechanism

Photolysis reactions: NO_2, O^1D, O^3P, HCHO, HNO_3 (out of total 39 reactions)

Example of O^1D quantum yield as function of wavelength and temperature

$$\Phi(\lambda,T)=\left\{\frac{q_1}{q_1+q_2}\right\}\times A_1\times\exp\left\{-\left(\frac{X_1-\lambda}{\omega_1}\right)^4\right\}+\left\{\frac{q_2}{q_1+q_2}\right\}\times A_2\times\left\{\frac{T}{300}\right\}^2\exp\left\{-\left(\frac{X_2-\lambda}{\omega_2}\right)^2\right\}$$
$$+A_3\times\left\{\frac{T}{300}\right\}^{1.5}\exp\left\{-\left(\frac{X_3-\lambda}{\omega_3}\right)^2\right\}+c$$

Non-photolysis reactions: updated 40 reactions, including 11 new reactions describing HNO_3 branching effect, CH_4 chemistry, and new reactions taken from the newer SAPRC11 mechanism.

New chemical species: HCOCO3, PHEN, XYNL, CATL (introduced in SAPRC11)

SAPRC07 Improvements: HNO_3 branching effect

$HO_2 + NO \rightarrow OH + NO_2$	(1)	$k(298\ K) = 8.8 \times 10^{-12}$
$HO_2 + NO + H_2O \rightarrow HNO_3 + H_2O$	(2)	$k(298\ K) = 1.6 \times 10^{-14}$

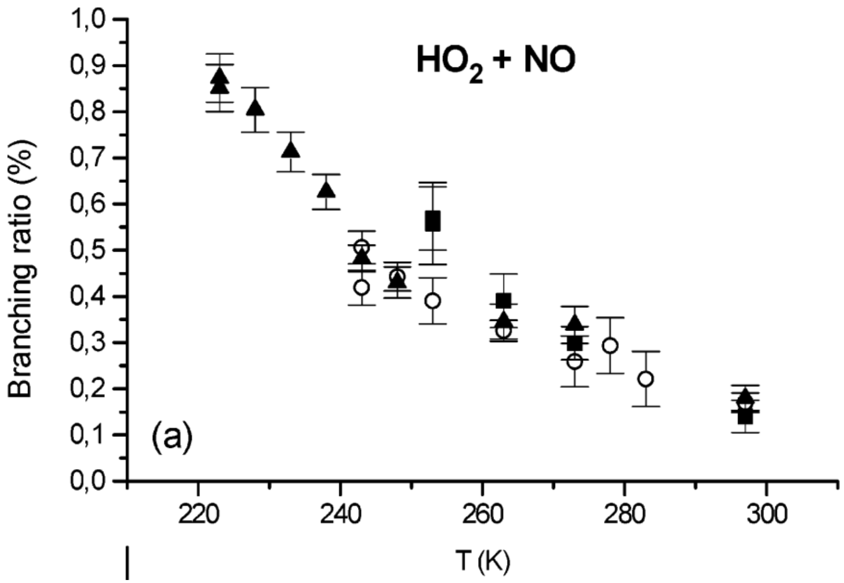
Reaction (2) plays as termination of HO_2 and NO and by that leads to decrease in O_3 formation.

At 298 K, reaction (2) is only ~ 0.2% as fast as reaction (1); reaction (2) is not considered in up-to-date chemical mechanisms.

Formation of HNO_3 increases under low temperature condition

Branching ratio (2)/(1) increase by 5-folds as temperature decrease from 298 K to 223 K [1]

HNO_3 branching effect was added into SAPRC07 mechanism for winter O_3 study.



(Ref: Figure 8, Butkovskaya et al., 2005)

[1]*Butkovskaya, N. I.; Kukui, A.; Pouvesle, N.; Le Bras, G.,* ***Formation of Nitric Acid in the Gas-Phase HO_2 + NO Reaction: Effects of Temperature and Water Vapor****. The Journal of Physical Chemistry A* ***2005,*** *109 (29), 6509-6520.*

SAPRC07 Improvements: Methane chemistry

Major O^1D reaction pathway:

$H_2O + O^1D = 2*OH$	(3)	$k = 2.14 \times 10^{-10}$

O^1D also reacts with CH_4:

$CH_4 + O^1D = OH + CH_3$	(4)	$k = 1.05 \times 10^{-10}$
$CH_4 + O^1D = HCHO + H_2$	(5)	$k = 7.5 \times 10^{-12}$
$CH_4 + O^1D = CH_2OH + H$	(6)	$k = 3.45 \times 10^{-11}$
$CH_2OH + O_2 = HCHO + HO_2$	(7)	$k(T) = 5.3 \times 10^{-12} \exp(170/T)$

- Reactions (4) through (7) form radicals and formaldehyde (HCHO) that have high O_3 reactivity
- Reactions (4) through (7) are not considered in up-to-date chemical mechanisms because of the abundance of water vapor over CH_4

$$[H_2O] \sim 10^4 \text{ ppm} \quad \text{vs.} \quad [CH_4] \sim 2 \text{ ppm}$$

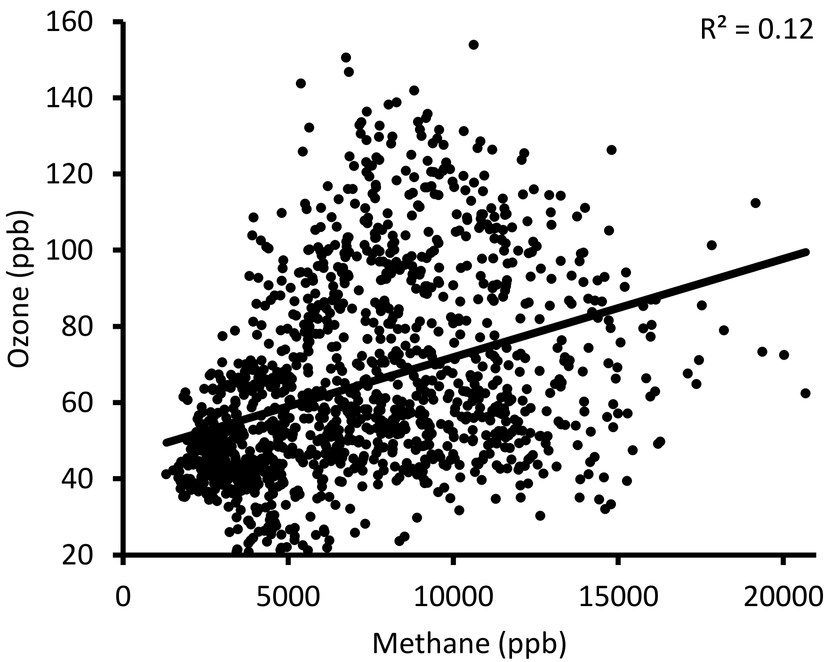
- Currently CH_4 is treated with constant concentration of 1.85 ppm in SAPRC07.

SAPRC07 Improvements: Methane chemistry (cont.)

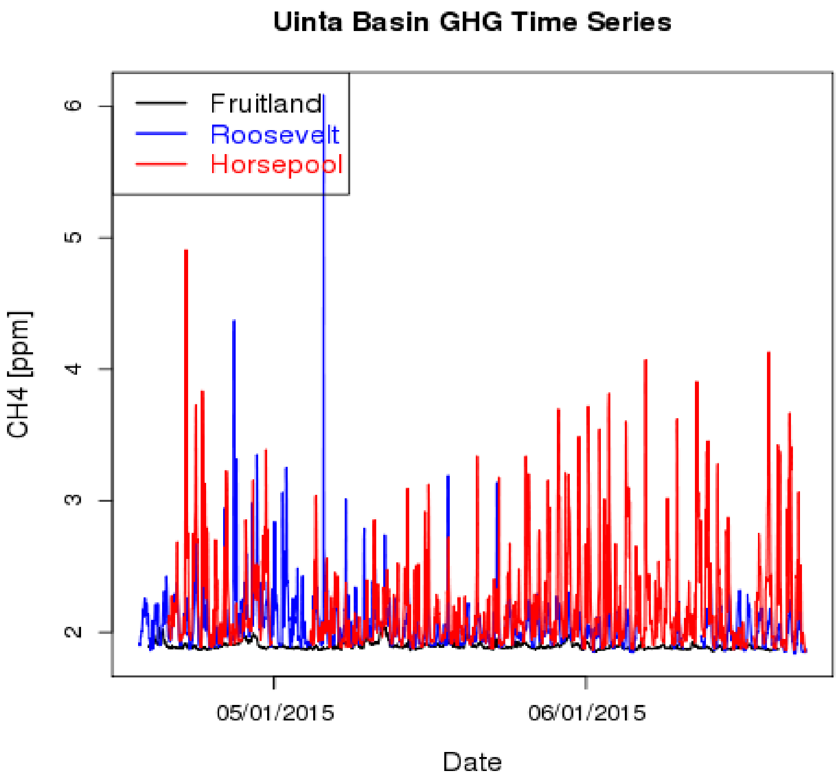
For Uintah basin in winter time:

- CH_4 concentrations are higher in the Uintah basin: ~ 10 – 20 ppm near surface layer under inversion conditions.
- Less water vapor under dry conditions during winter: $[H_2O] \sim 10^3$ ppm at the surface layer

Observed CH_4 at Horsepool monitoring site (Dec 2012 – March 2013)



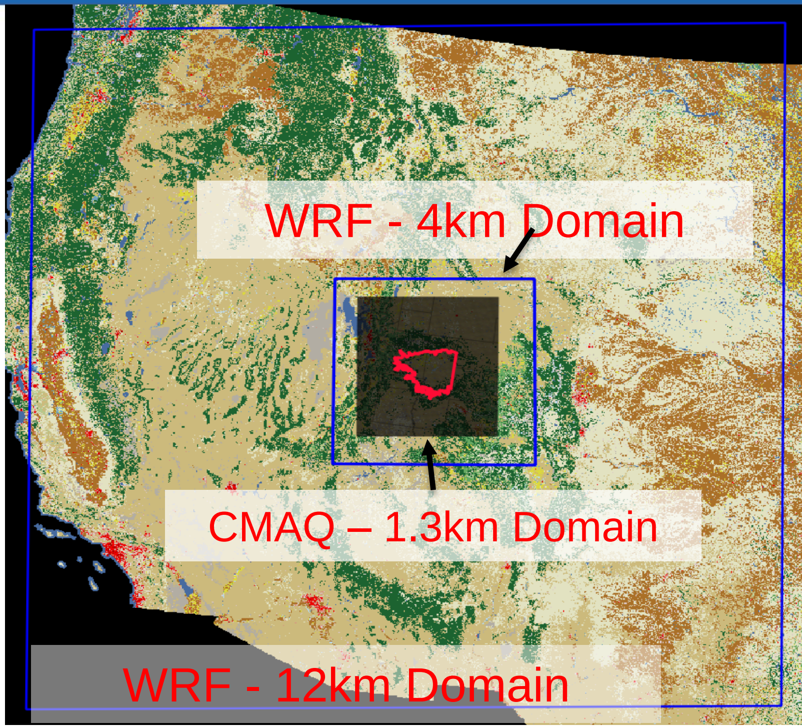
Courtesy to Seth Lyman – Utah State University



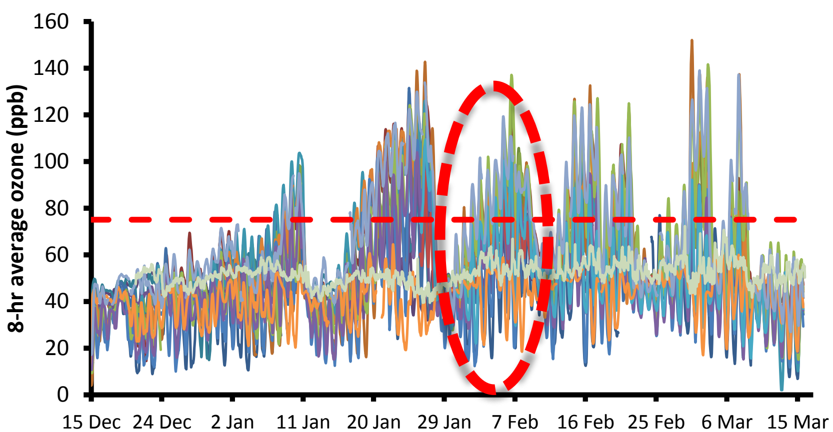
Courtesy to John Lin – University of Utah

Reactions with CH_4 are added to the SAPRC07 chemical mechanism. Furthermore, CH_4 concentrations are estimated instead of being kept at constant background concentration of 1.85 ppm

Model configurations



Simulation episode: 01/29 – 02/07 2013



Weather Research and Forecasting (WRF) model version 3.5

Community Multiscale Air Quality (CMAQ) version 5.0.2 with modifications:

- Surface albedo
- Ozone dry deposition over snow

Utah BLM ARMS Emission Inventories for base year 2010, with modifications.

Sensitivity simulations:

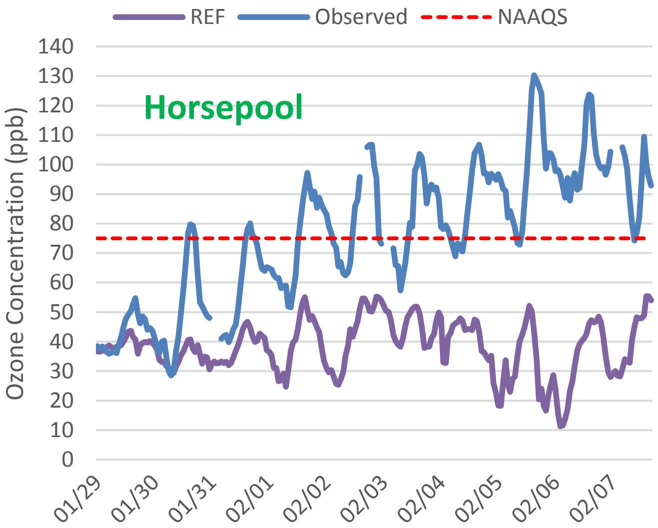
REF: non-updated SAPRC07

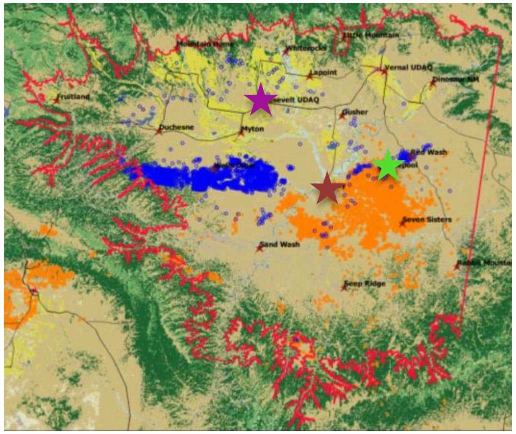
NITRIC: SAPRC07 updated with HNO_3 branching

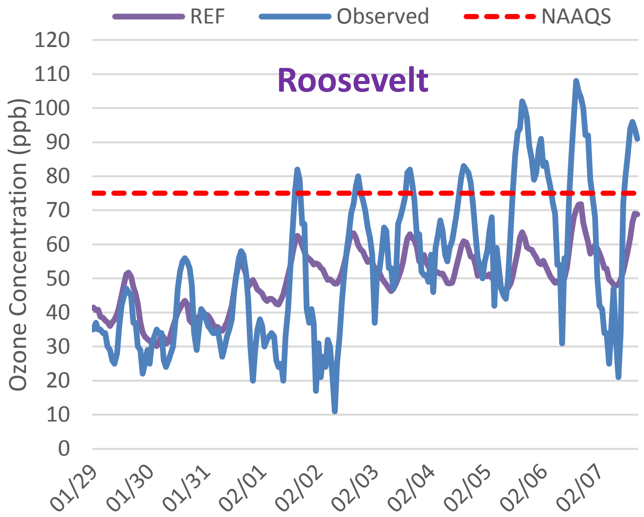
METHN: SAPRC07 updated with CH_4 chemistry

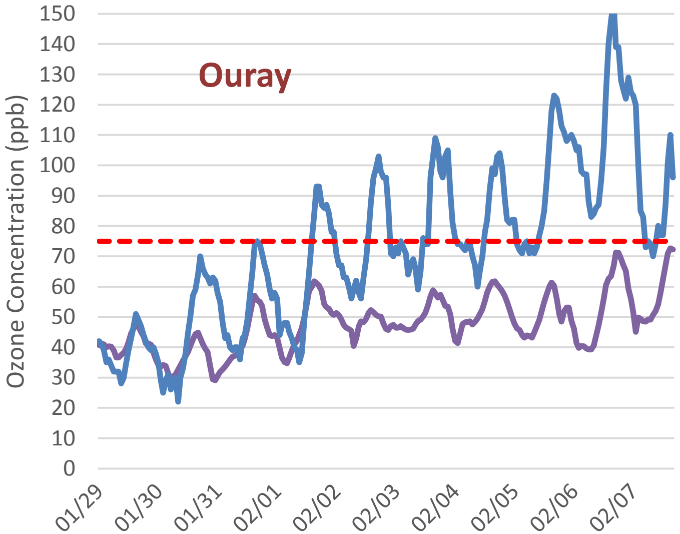
ALL: SAPRC07 with all updates

Model performance: Ozone concentrations are underestimated









Reasons:

- Incomplete emission inventory (VOC is too low?)
- Lack of representative VOC speciation profiles for oil & gas
- WRF model has difficulties in simulation cold air pool (too deep mixing layer)
- Discrepancies in chemical mechanism

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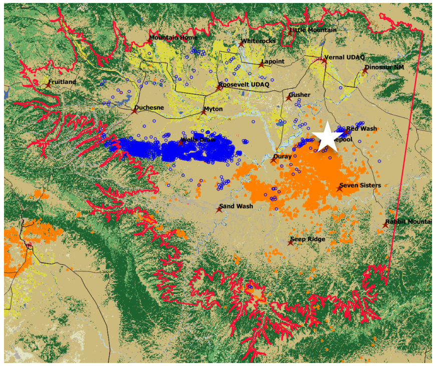
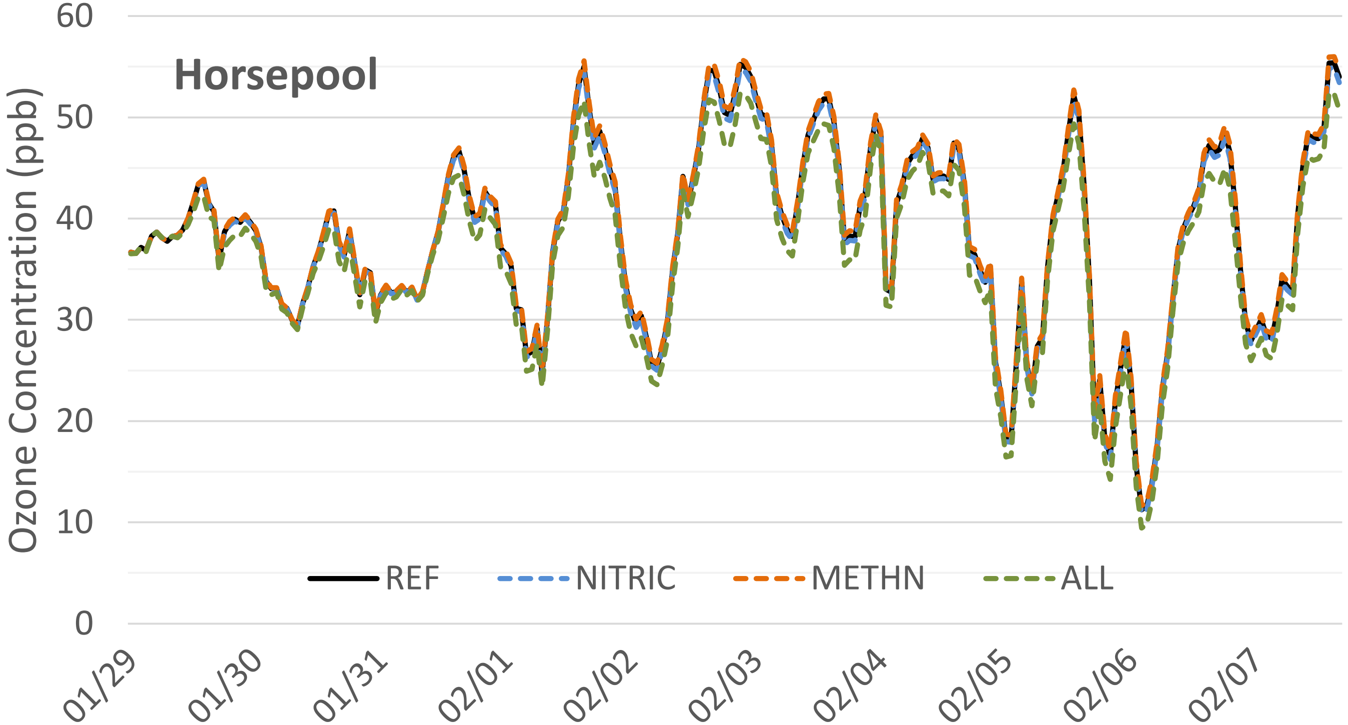
Updated-SAPRC07 evaluation





O_3 comparison: 01/29 – 02/07 2013 (ppb)

	REF	NITRIC	METHN	ALL
Overall average	38.4	38.0	38.7	36.7
Highest concentrations	55.4	54.8	56.0	52.4
Highest 8hour-average	53.2	52.6	53.7	50.1
Maximum difference (-REF)	---	-0.6	0.8	-3.6

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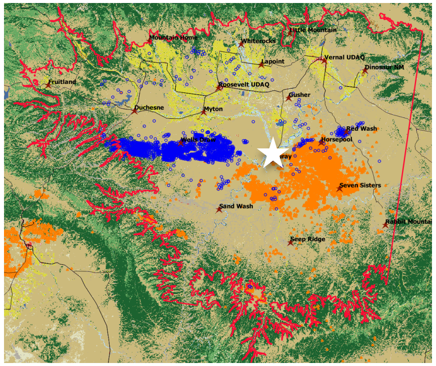
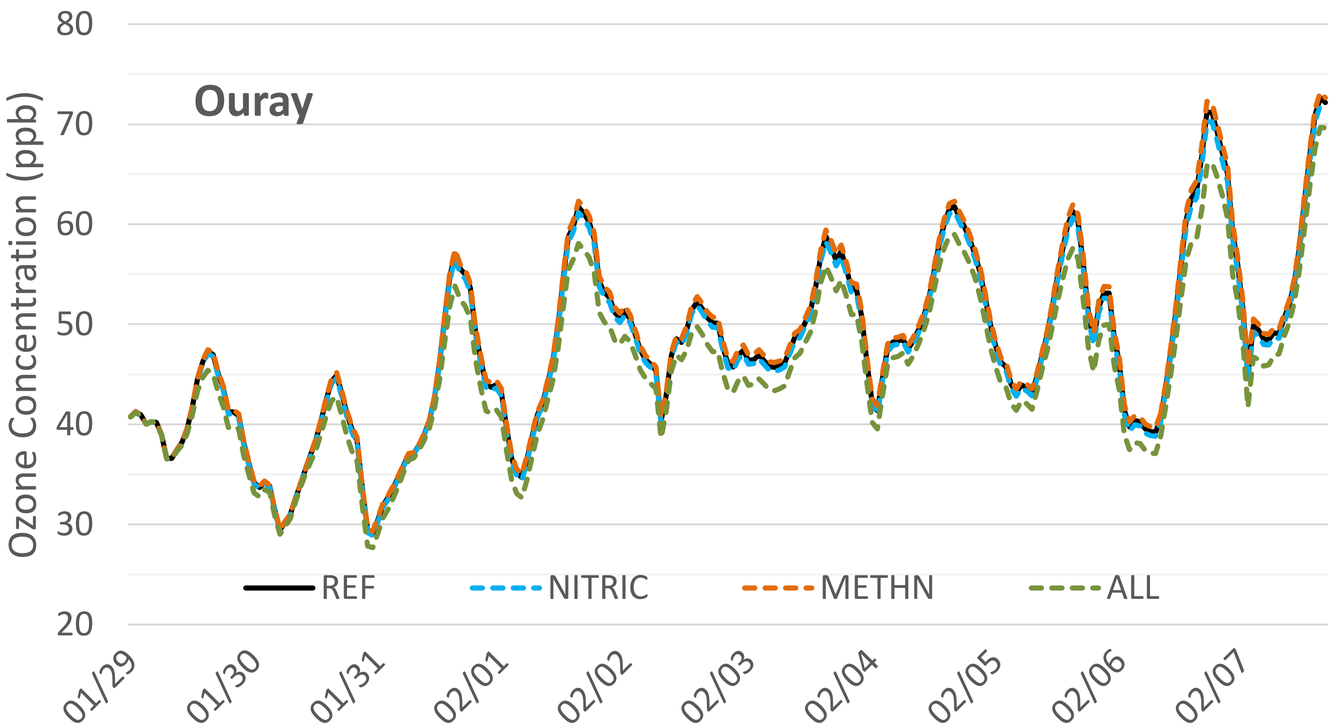
Updated-SAPRC07 evaluation





O_3 comparison: 01/29 – 02/07 2013 (ppb)

	REF	NITRIC	METHN	ALL
Overall average	47.5	47.2	47.9	45.4
Highest concentrations	72.6	71.9	73.2	69.6
Highest 8hour-average	67.1	66.2	68.0	62.3
Maximum difference (-REF)	---	-0.96	1.1	-5.4

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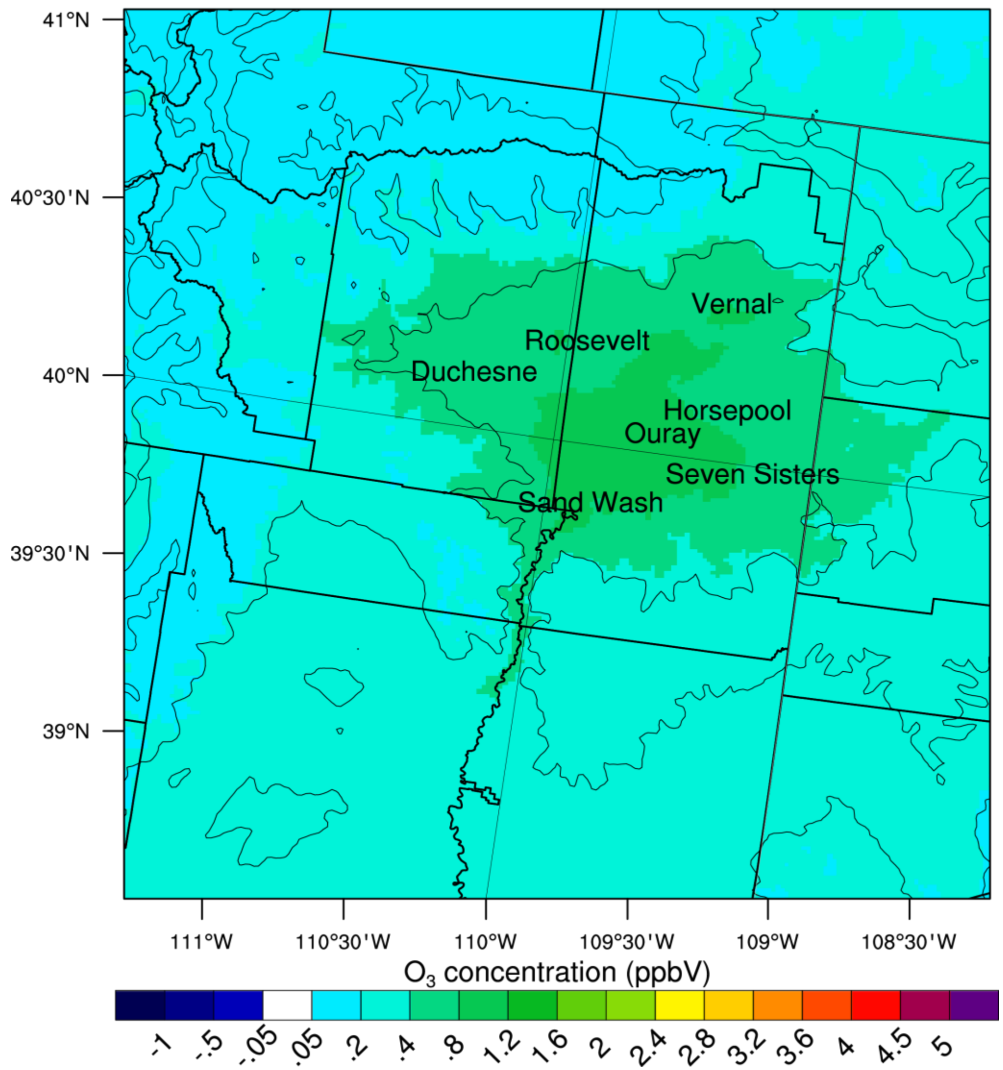
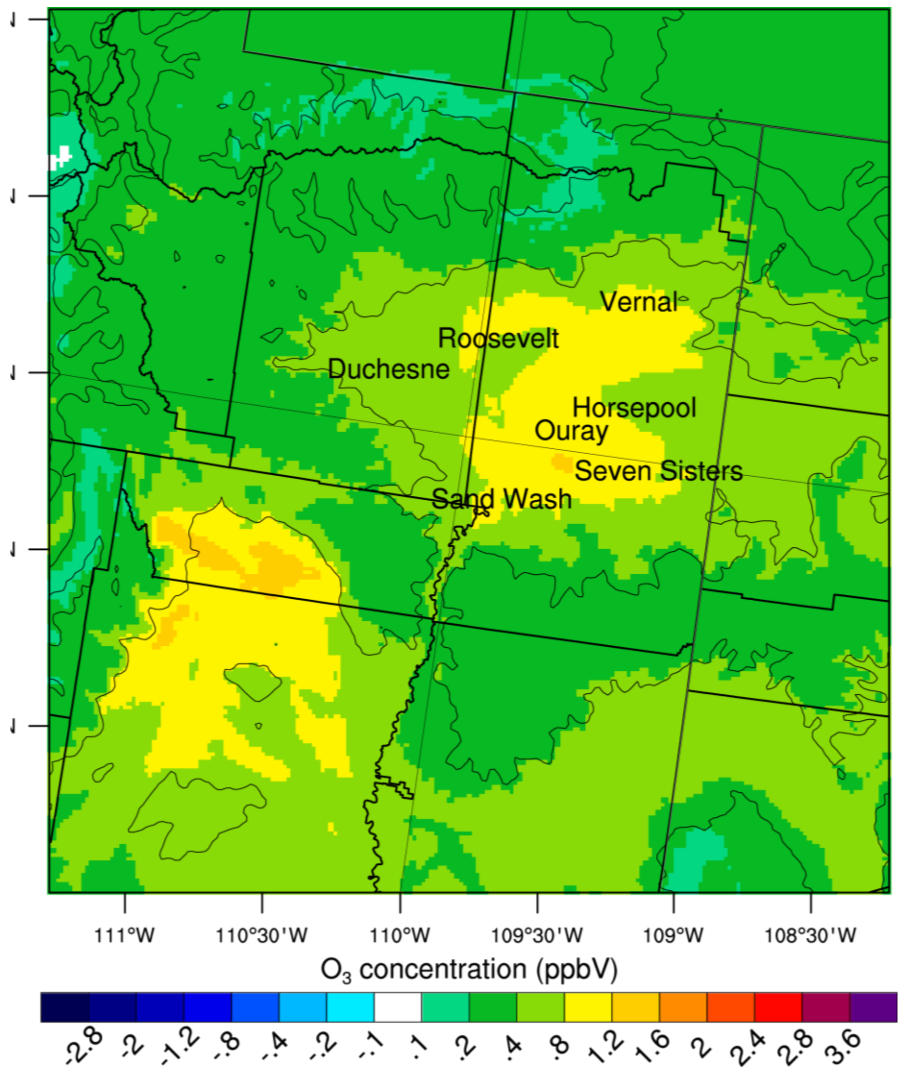
Updated-SAPRC07 evaluation

Maximum differences

REF – NITRIC: Decreases O_3 production



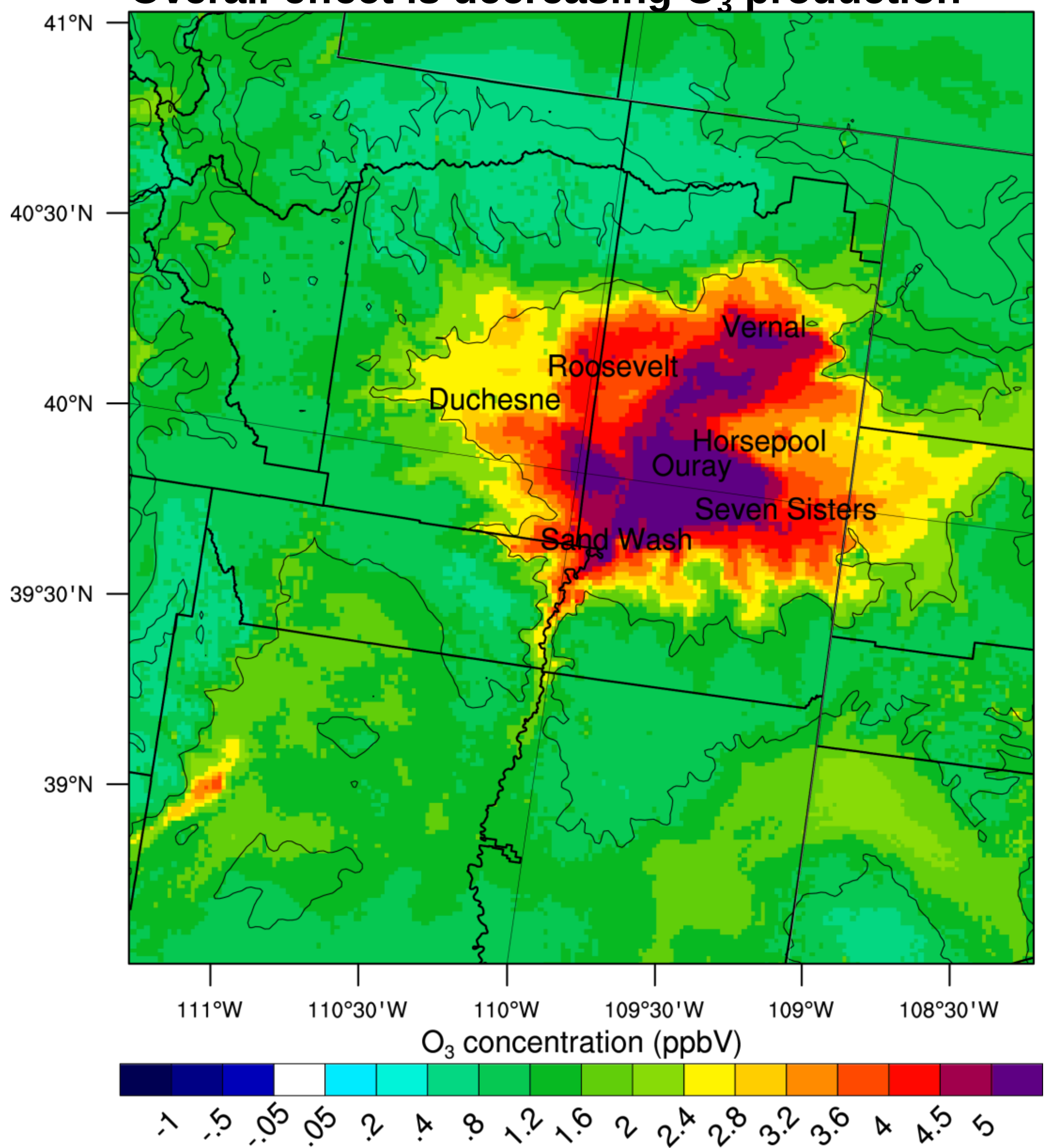
METHN - REF: Increases O_3 production



Updated-SAPRC07 evaluation

REF – ALL

Overall effect is decreasing O_3 production



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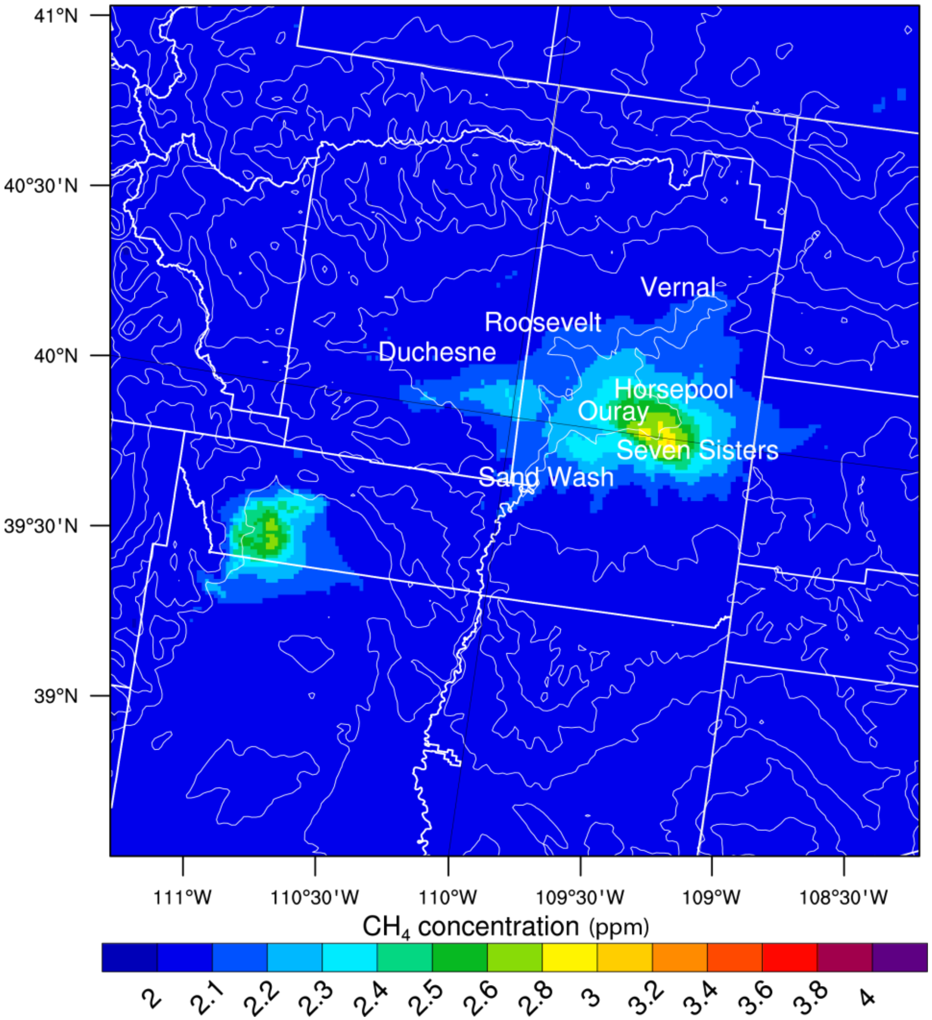
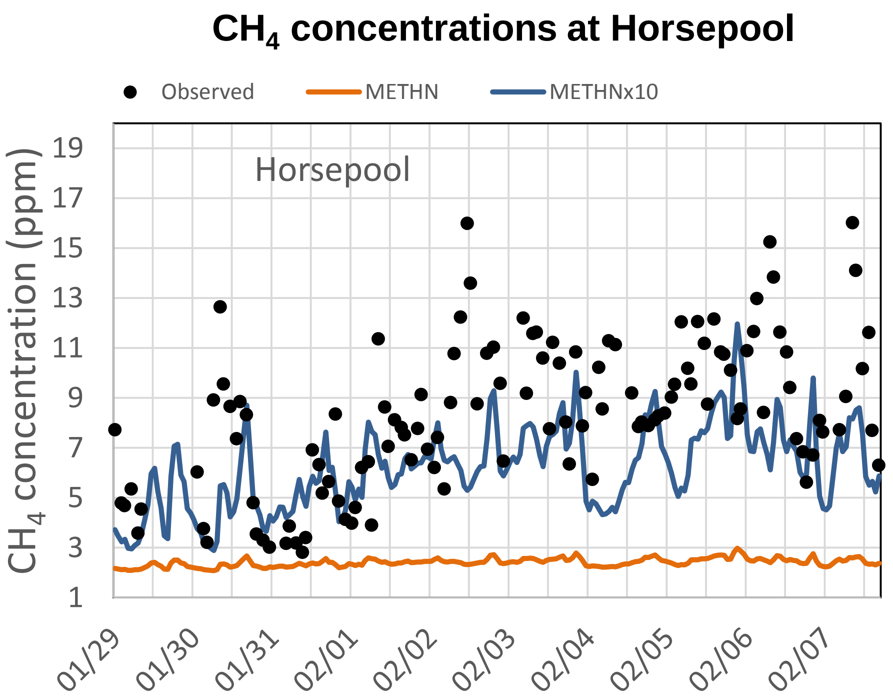
Updated-SAPRC07 evaluation: CH_4 performance





- Simulated CH_4 concentration highly underestimated observed values
- Arbitrary increase of CH_4 emission by 10 times resulted in simulated CH_4 concentrations closer but still underestimated observed CH_4

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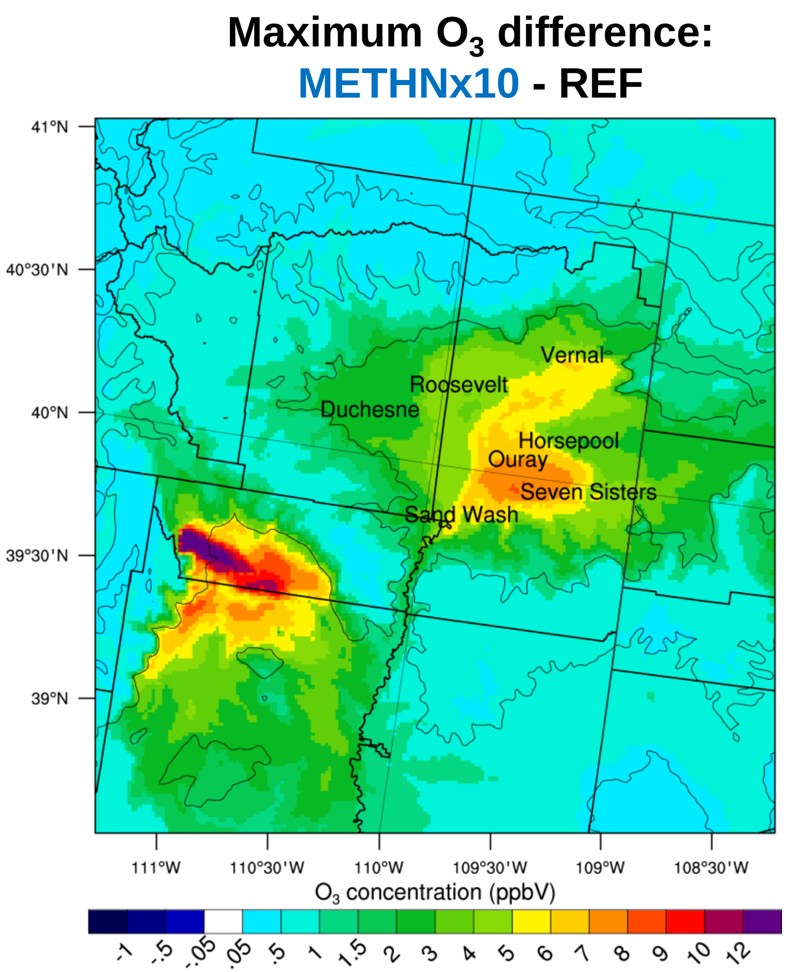
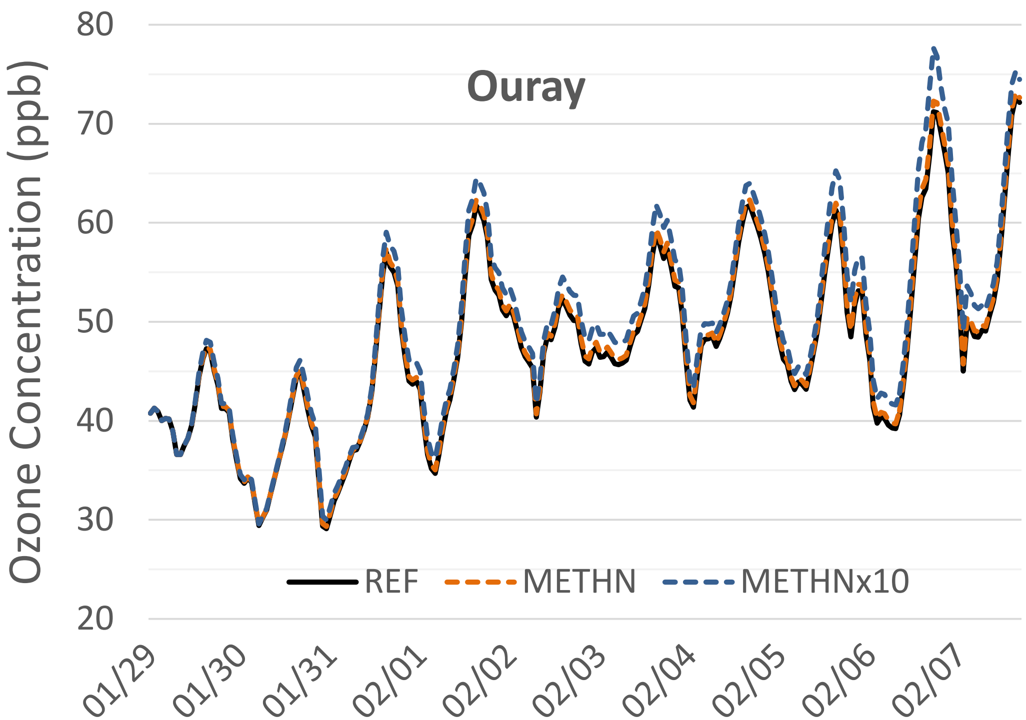
Updated-SAPRC07: Arbitrary increase of CH_4 emission by 10 times significantly increased O_3 concentrations





O_3 comparison: 01/29 – 02/07 2013 (ppb)

	REF	METHN	METHNx10
Overall average	47.5	47.9	**49.9**
Highest concentrations	72.6	73.2	**77.7**
Highest 8hour-average	67.1	68.0	**72.7**
Maximum difference (-REF)	---	1.1	**6.9**

Summary

- The SAPRC07 chemical mechanism has been improved for simulating winter ozone episodes in Uintah basin.

- Impact of introduction of HNO_3 branching effect is marginal: O_3 production decreased by up to 1 ppb.

- CH_4 chemistry is important for O_3 production in Uintah basin during wintertime: O_3 production increased by up to 1.6 ppb with “as is” CH_4. Increase of CH_4 emission significantly increases O_3 production.

- Combination of all modifications to SAPRC07 resulted in decrease of O_3 production. This effect likely will change with improved emission inventory.

- Improvement of emission inventory is a critical need. This improvement should include developments of VOC speciation profiles that represent well the oil and gas emissions.